REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
	Technical Paper	

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER F04611-99-C-0025
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 1011
	5e. TASK NUMBER 001V
	5f. WORK UNIT NUMBER 549882
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030128 105

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Leilani Richardson
a. REPORT	b. ABSTRACT	c. THIS PAGE	A		19b. TELEPHONE NUMBER *(include area code)*
Unclassified	Unclassified	Unclassified			(661) 275-5015

10/10010

MEMORANDUM FOR PRS (In-House Contractor Publication)

FROM: PROI (STINFO) 29 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2002-089** Jerry Boatz (PRSP) and Karl Christe (ERC), "New Polynitrogen Molecules – Energetic 'Air' as a Next-Generation Propellant?"

DoD HPC Success Story Booklet **(Statement A)**

Title: New Polynitrogen Molecules -- Energetic "Air" as a Next-Generation Propellant?

Authors: Jerry A. Boatz and Karl O. Christe
Air Force Research Laboratory
AFRL/PRSP
10 E. Saturn Blvd.
Edwards AFB, CA 93524-7680
voice: 661-275-5364
fax: 661-275-5471
email: jerry.boatz@edwards.af.mil

Alternate POC: Karl O Christe
Air Force Research Laboratory
AFRL/PRSP
10 E. Saturn Blvd.
Edwards AFB, CA 93524-7680

Affiliation: Air Force Research Laboratory, Edwards AFB

Program Supported: High Energy Density Materials
Program Manager: Dr. Gregory Drake
Air Force Research Laboratory
AFRL/PRSP
10 E. Saturn Blvd.
Edwards AFB, CA 93524-7068
voice: 661-275-5355

HPC Resource Environments: IBM SP/P3 at ASC, SGI Origin 3800 at AFFTC

The identification, development, and formulation of new energetic materials for advanced rocket propulsion applications is an area of long standing interest to the Air Force. The performance limits of currently used propellants have been reached, so new energetic compounds are required to significantly improve the ability of the warfighter to access and control space.

Polynitrogen species such as the recently discovered N_5^+ cation are of interest as potential energetic ingredients in new propellant formulations. The recent successful synthesis of N_5^+ in macroscopic quantities has prompted the search for additional polynitrogen compounds. Computational chemistry plays a central role in determining the stabilities, potential synthetic pathways, and key spectroscopic "fingerprints" of new polynitrogen species.

Conventional techniques for characterizing new materials such as polynitrogens have relied heavily on costly and time-consuming experimental synthesis and characterization. However, the availability of HPC resources has significantly lessened the need for these more empirical approaches by enabling the application of reliable high-level quantum chemical calculations to reliably predict important properties such as heats of formation, stabilities, mechanisms of formation and decomposition, and spectroscopic constants. A key advantage of using HPC in

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

this regard is the ability to efficiently "screen" a large number of potential polynitrogen molecules and focus subsequent experimental efforts on the subset of only the promising candidates.

The structures, stabilities, vibrational frequencies, and infrared intensities of several potential synthetic precursors to new polynitrogen species have been computed using ab initio electronic structure theory, at the second order perturbation theory level (MP2, also known as MBPT(2)), using the 6-31G(d) valence double-zeta polarized basis set. Shown in the accompanying figure is the predicted structure of triphenylmethyldiazonium cation, also known as trityldiazonium, which is a possible precursor to new polynitrogen compounds such as pentazole, a 5-membered ring system. The calculated structure shows that this cation is unstable with respect to dissociation of N_2. Therefore, these calculations predict that this cation is not a viable polynitrogen precursor.

Although this is a negative result in the sense that it indicates that trityldiazonium is not a stable precursor, it is nonetheless a highly useful result in multiple ways. First, it saves significant time and effort by eliminating from consideration for subsequent attempts at synthesis a compound which is not likely to be stable. Furthermore, it suggests ways in which the trityldiazonium cation may be chemically modified in order to overcome its instability (e.g., by judicious placement of electron-withdrawing groups on the trityl moeity.) Future work in this area will examine such derivatives of the trityldiazonium cation, as well as other classes of promising polynitrogen precursors.

Primary CTA: CCM

Scientific visualization: WebLabViewerLite for visualization of optimized geometries.

References: (1) K.O. Christe, W.W. Wilson, J.A. Sheehy, and J.A. Boatz, "A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material", Angew. Chem. Int. Ed. 38, 2004-2009(1999).

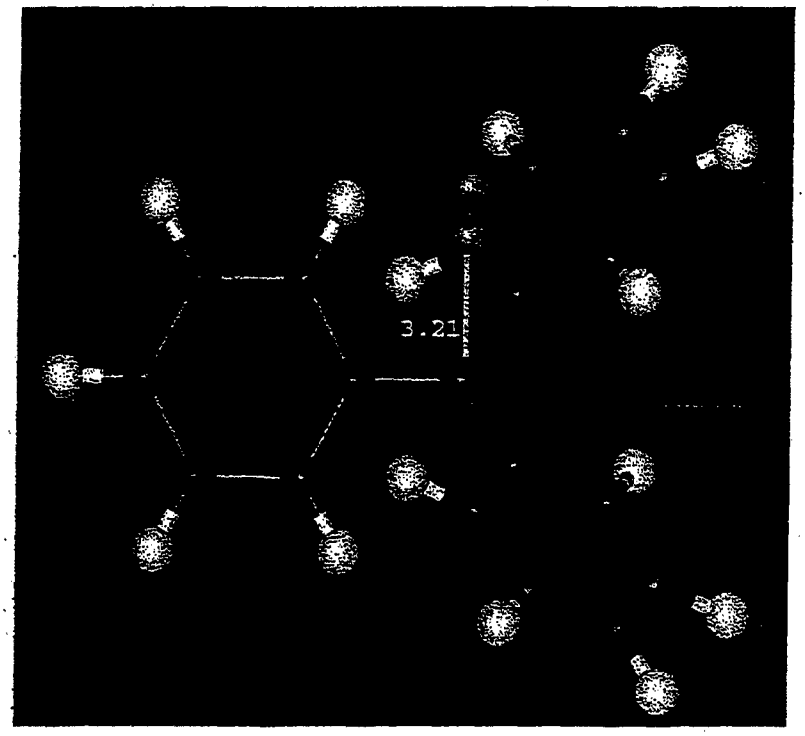

Figure Caption: MP2/6-31G(d) optimized structure of triphenylmethyldiazonium cation, $[C_{19}N_2H_{15}]^+$. The predicted C-N internuclear distance of 3.21 angstroms indicates that this cation is unstable with respect to dissociation to triphenylmethyl cation and N_2.

Acronyms:

MP2	Moller-Plesset perturbation theory (second order)
MBPT(2)	Many-body perturbation theory (second order).